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Synthesis and Reactivity of Silyl-Ketene Acetal-Modified Polysiloxanes
Preparation of Polysiloxanes with High Dielectric Constraints

by

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**SYNTHESIS AND REACTIONS OF SILYL KETENE
ACETAL-MODIFIED POLYSILOXANES. PREPARATION OF
POLYSILOXANES WITH HIGH DIELECTRIC CONSTANTS**

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Abstract

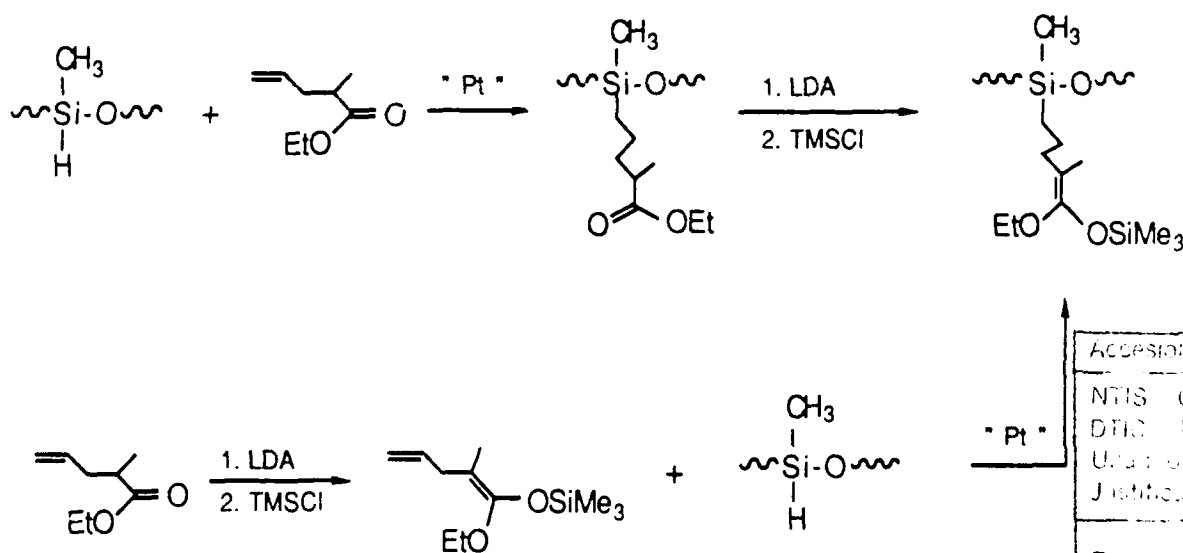
A new route to the functionalization of polysiloxanes is described. Silicones having pendant silyl ketene acetals are synthesized through hydrosilation of polymethylhydrosiloxane with a terminal olefin bearing a silyl ketene acetal or, alternatively, a terminal olefin-ester which can be subsequently converted to the ketene acetal. The polysiloxanes can be reacted with the electrophiles such as p-nitrobenzenesulfonyl chloride, affording derivatives having highly polar pendants. These materials have dielectric constants as high as 9 and dissipation factors of 0.02-0.06 at 100kHz at room temperature. The temperature dependencies of the dielectric constants are a function of polar pendant group concentration.

Keywords: synthesis, polysiloxanes, silicones, chemical modification, dielectric properties

Introduction

Polysiloxanes, or silicones, have received much attention as specialty polymers since their commercial application in 1940's and are by far the most important of the inorganic backbone polymers. Special interest in these systems has developed as a result of their unique properties, which include low glass transition temperatures, good thermal and oxidative stability, low surface energies, excellent biocompatibility, and high gas permeabilities.^{1,2}

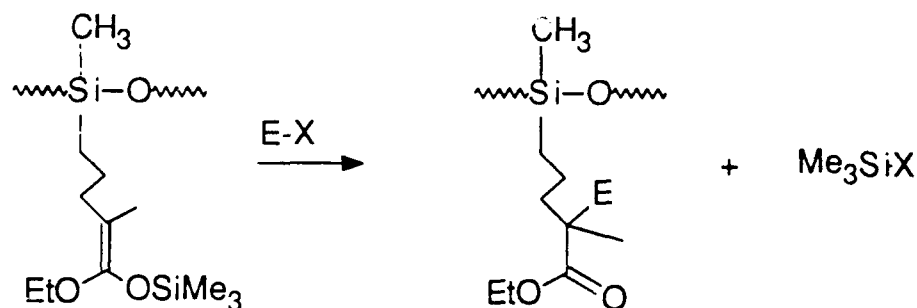
The hydrosilation reaction, because of its typically high yield, enjoys frequent utility as a route to functionalized silicones.² However, the range of materials which can be synthesized is often limited by the range of terminal olefins which can be purchased or easily prepared. We wish to report a variant of this approach which introduces silyl ketene acetal groups for subsequent reaction with a variety of electrophiles, preliminary accounts of which have appeared elsewhere.^{3,4} The latter reaction, like hydrosilation, affords high yields with appropriately chosen substrates⁵ and is thus attractive as a polymer modification reaction. As indicated in Scheme 1, poly(methylhydrosiloxane) can be derivatized with silyl ketene acetal groups by one of two routes.



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An ester bearing a terminal olefin, such as ethyl 2-methyl-4-pentenoate, can be first transformed into the corresponding silyl ketene acetal and then used for hydrosilation. Alternatively, hydrosilation with the ester can be accomplished first, followed by transformation to the silyl ketene acetal. In addition, copolymers are readily prepared by hydrosilation with a mixture of the ketene acetal and ethyl 2-methyl-4-pentenoate.

We report here the details of the synthesis of the silyl ketene acetal-modified polysiloxanes and their reactions with selected electrophiles (Scheme 2) such as 4-nitrobenzenesulfonyl chloride. The



Scheme 2

resulting polysiloxanes have highly polar side groups and thus may have large dielectric constants over a broad frequency range. Preliminary results will be presented later which support this contention. Another motivation for the preparation of these materials is that they may serve as new electrolyte hosts which, because of a large dielectric constant, are able to increase ion pair dissociation compared with oligoether pendants. We also note that as silyl ketene acetals are excellent initiators for the polymerization of methacrylates and related monomers,⁶ the ketene acetal-derivatized polysiloxanes may be employed for the preparation of new silicone graft and comb copolymers or, using cyclic oligomers or end-functionalized materials, star and block copolymers respectively. This chemistry however will be the subject of another paper.

Experimental

A. Materials: Poly(methylhydrosiloxane), PMHS, was acquired from Petrarch, and was found by ^{200}H NMR to have a number-average molecular weight of approximately 4500 g/mol according to the supplier. Ethyl 2-methyl-4-pentenoate and dimethylmethoxy(trimethylsilyl)ketene acetal, DMTA, were acquired from Aldrich and distilled prior to use. Chloroplatinic acid, 4-nitrobenzenesulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, and 4-nitrobenzoyl chloride were acquired from Aldrich, and stored in a refrigerator. Tetrahydrofuran and toluene were refluxed over sodium benzophenone radical anion and calcium hydride, respectively, and distilled just prior to use. Methylene chloride and diethyl ether were distilled prior to use. Trimethylsilylchloride was distilled prior to use.

B. Model Reactions: We have investigated the reaction of DMTA with 4-nitrobenzenesulfonyl chloride, 2,4-dinitrobenzenesulfonyl chloride, and 4-nitrobenzoyl chloride as model systems. Representative conditions follow.

a. DMTA with 4-nitrobenzenesulfonyl chloride:

To a solution of 4-nitrobenzenesulfonyl chloride (8.1 g, 42 mmol) in 100ml dry ether, DMTA (8.5 ml, 42 mmol) was added. The mixture was refluxed under argon for 30 min. Ether was removed using a rotary evaporator and then the product was distilled at reduce pressure (b. p. $138-140^{\circ}\text{C}/4\text{mm Hg}$). The yield of methyl-2-methyl-2-(4-nitrothiophenoxy)propionate was 99%.

This material will be referred to as MNTP. ^1H NMR (CDCl_3), δ (in ppm from TMS): 8.16 (q, 2H, Ar), 7.56 (q, 2H, Ar), 3.68 (s, 3H, OCH_3), 1.52 (s, 6H, 2CH_3). MS (256).

b. DMTA with 2,4-dinitrobenzenesulfonyl chloride:

To a solution of 2,4-dinitrobenzenesulfonyl chloride (2.3g, 9.8mmol) in 25ml dry methylene chloride, DMTA (2 ml, 9.8mmol) was added. The mixture was refluxed under argon for 40 min. Methylene chloride was removed under reduce pressure, and methyl 2-methyl-2-(2,4-dinitrothiophenoxy)propionate was obtained as yellow crystals (mp $82-86^{\circ}\text{C}$). The yield was 95%. ^1H

NMR (CDCl_3) δ (in ppm from TMS) 8.89 (d, 1H, Ar), 8.33 (q, 1H, Ar), 7.63 (d, 1H, Ar), 3.75 (s, 3H, OCH_3), 1.68 (s, 6H, 2CH_3). MS (301).

c. DMTA with 4-nitrobenzoyl chloride:

To a solution of 4-nitrobenzoyl chloride (5.6g, 30mmol) in 80ml dry ether, DMTA (6 ml, 30mmol) was added. The mixture was refluxed under argon for 24 hr. Ether was removed under reduce pressure, and 2-methyl-2-(4-nitrobenzoyl)propionate was obtained as yellow crystals (mp 62-64 $^{\circ}\text{C}$). The yield was 95%. ^1H NMR (CDCl_3) δ (in ppm from TMS) 8.27 (d, 2H, Ar), 7.95 (d, 2H, Ar), 3.64 (s, 3H, OCH_3), 1.53 (s, 6H, 2CH_3). MS (252).

C. Synthesis of Ethyltrimethylsilyl-2-Methyl-2-Allylketene Acetal (ETMA):

A 500ml three-necked round bottomed flask was fitted with a reflux condenser, magnetic stirring bar, rubber septum, and a gas inlet. The apparatus was connected through the gas inlet to a argon source and reflux condenser to a bubble. After the flask was flame-dried and flushed with argon, it was charged with 250ml of THF and 30.2ml (214.9mmol) of distilled diisopropylamine. The flask was immersed in a ice-salt bath and cooled to -10°C , and over a period of about 5 min, 86.0ml (214.9mmol) of 2.5M n-butyllithium in hexane was added dropwise, with continuous stirring, with a syringe through the septum. After an additional 20 min of stirring, ethyl 2-methyl-4-pentenoate 35ml (214.9mmol) was added dropwise through additional funnel over a 10 min period, the solution was stirred for an additional 30 min at 0°C . At this point, 40.9ml (322.1mmol) of distilled trimethylsilylchloride was rapidly introduced with a syringe through the septum. After the addition was completely (ca 30 sec) the solution was stirred for an additional 1 hr at room temperature. Solvent was removed using a rotary evaporator and the residue was treated with 200 ml of pentane. The slurry was filtered and filtrate was concentrated on a rotary evaporator and then distilled at reduce pressure. The product, ethyltrimethylsilyl-2-methyl-2-allylketene, distilled at 79°C (15mmHg). The yield was 97%. ^1H NMR (CDCl_3) δ (in ppm from TMS) 5.70

(m, 1H, allyl), 4.96 (m, 2H, allyl), 3.70 (m, 2H, OCH_2CH_3), 2.68 (q, 2H, $-\text{CH}_2-$), 1.47 (d, 3H, CH_3), 1.19 (m, 3H, OCH_2CH_3), 0.19 (d, 9H, SiMe_3).

D. Hydrosilation of Poly(methylhydrosiloxane) with ETMA:

To a mixture of PMHS (6g, 100mmol) and ETMA (21.4g, 100mmol) in 100ml dry toluene, H_2PtCl_6 (40mg in 0.5ml isopropanol) was added. The mixture was refluxed under argon at 50°C for 18-24h. The extent of reaction was followed by IR spectroscopy. After the Si-H peak in the IR spectrum disappeared, solvent and unreacted ETMA were removed under reduce pressure with rotary evaporator first, and the resulting liquid was kept under high vacuum for 24 hr. ^1H NMR indicated that the extent of hydrosilation was $> 97\%$. The product, poly[(5-ethoxy-5-trimethylsiloxy-4-methylpropyl-4-ene)methylsiloxane], was a colorless, viscous liquid. [^1H NMR (CDCl_3)

δ (in ppm from TMS) 3.71(q, 2H, OCH_2CH_3), 1.90(t, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.48(s, 3H, CH_3),

1.33(m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.14(t, 3H, OCH_2CH_3), 0.43(t, 2H, SiCH_2), 0.15(s, 9H,

SiMe_3), 0.02(s, 3H, $\text{Si}(\text{CH}_3)\text{O}$]. It will be referred to as PSi-SKA. We also prepared the wholly pendant ester derivative, poly[5-ethoxy-4-methylpropyl-5-one)methyl siloxane, by hydrosilation with ethyl-2-methyl-4-pentenoate under similar conditions; this is referred to as

PSi-Ester. [^1H NMR (CDCl_3) δ (in ppm from TMS) 4.09(q, 2H, OCH_2CH_3), 2.37(m, 1H,

$\text{CH}(\text{CH}_3)$), 1.65(m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.34(m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.25(t, 3H,

OCH_2CH_3), 1.17(d, 3H, $\text{CH}(\text{CH}_3)$), 0.46(t, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 0.02(s, 3H, $\text{Si}(\text{CH}_3)\text{O}$].

Copolymers containing various percentages of pendant silyl ketene acetal functionality, with the remainder the corresponding ester, were synthesized using the same procedure with appropriate ratios of ETMA and ethyl-2-methyl-4-pentenoate. These are termed PSi-SKA-co-Ester.

E. Reactions of Ketene Acetal-Modified Polysiloxane with Electrophiles:

The polysiloxanes having ketene acetal pendants can be reacted with various electrophiles. A procedure for derivatizing the copolymer containing approximately 75% pendant silyl ketene acetals with either 4-nitrobenzenesulfonyl chloride or 2,4-dinitrobenzenesulfonyl chloride is described here as a representative example.

To a solution of 16.3g (64mmol) of S-70 in 250ml dry ether, 4-nitrobenzenesulfonyl chloride (8.87g, 46.8mmol) or 2,4-dinitrobenzenesulfonyl chloride (10.98 g, 46.8mmol) was added slowly. The mixture was stirred under argon at 40°C for 30 min. Then solvent was removed at reduce pressure. The residue was washed with ether several times in order to remove unreacted sulfonyl chloride, and then was dried under reduced pressure for 2 days. Both products were orange liquids, though the viscosity of the dinitrothiophenoxy derivative was much higher.

F. Elemental Analyses and Spectroscopic, Thermal and Dielectric Characterization:

Elemental analyses were performed by Schwarzkopf Laboratory, Woodside, N.Y. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer. IR spectra were obtained on a Perkin-Elmer 298 infrared spectrophotometer. The concentrations of polar pendant groups were calculated from ^1H NMR integrations and elemental analyses. Glass transition temperatures (T_g 's) were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate 20°C/min. Samples were dried overnight at 60°C prior to loading in the DSC pans. The T_g was taken at the inflection point in the DSC trace. Dielectric constants were measured at room temperature at 100kHz using a Balsbaugh liquid cell and GenRad 1689M RLC bridge. Measurements on water at 24-25°C afforded a dielectric constants (two separate measurements) of 77.8 and 78.6; it is reported to be 78.5 at 25°C.⁷ The silicones were loaded onto the bottom plate of the cell and any air bubbles were removed by mainting the sample in a vacuum oven for as long as necessary (typically 2 hr). For measurements of dielectric constants at elevated temperatures, a custom-built cell was employed which could be immersed in a constant-temperature bath. It was of a male-female type having a Teflon spacer and was constructed from stainless-steel. The capacity

of the cell was about 1 ml. This cell provided less accurate but reasonable data. For example, the dielectric constant of nitrobenzene was ca. 30.5 at 24-25°C and decreased to ca. 27.4 at 50°C using this cell. For comparison, it has been reported that the dielectric constant of nitrobenzene is 34.4 at 25°C and 30.2 at 50°C.⁸

Results and discussion

As a model system, we have investigated reactions of dimethylmethoxy(trimethylsilyl)ketene acetal with various electrophiles. The extent of reaction as well as the time required to reach maximum conversion are collected in Table 1. The silyl ketene acetal reacts readily the electrophiles shown (note that no catalyst is employed), and the yields are quite high. A longer reaction time was needed for 4-nitrobenzoyl chloride as compared with the sulfenyl chlorides. Incidentally, the highly polar liquid methyl-2-methyl-2-(4-nitrothiophenoxy)propionate has a dielectric constant of about 15 (0.1 kHz) which is invariant with frequency up to 100 kHz.

Hydrosilation of PMHS with ETMA or Ethyl 2-methyl-4-pentenoate proceeded in high yield as indicated by the absence of the Si-H stretch in the IR and the Si-H resonance in the ¹H NMR spectra, respectively. Figures 1a-c the ¹H NMR spectra of the parent polymethylhydrosiloxane, PSi-SKA, and PSi-Ester, respectively. The resonances of the ethyl group in the PSi-SKA are not well-defined due to the presence of E-Z isomers. Otherwise, the materials appear to be quite clean. Samples of PSi-SKA and various copolymers were treated with either 4-nitrobenzenesulfonyl chloride or 2,4-dinitrobenzenesulfonyl chloride. Figures 2 and 3 show the ¹H NMR spectra of a copolymer (ca. 70% SKA) and PSi-SKA after each was treated with 4-nitrobenzenesulfonyl chloride. Again, the former exhibits poorly resolved resonances for the ethyl group, although here it is because of two slightly different chemical shifts of the ethyls in the different repeat units. The highly derivatized polymer (ca. 93% nitrothiophenoxy groups) shows single, well-resolved resonances of the ethyl group (Figure 3).

Elemental analysis (EA) and NMR results for PSi-SKA-co-Ester materials reacted with either 4-nitrobenzenesulfonyl chloride (mononitro series, labeled as A) or 2,4-dinitrobenzenesulfonyl chloride (dinitro series, labeled as B) are presented in Table 2. The ratio of peak areas of the aromatic protons to the $-\text{CH}_2-$ protons of the ethoxy groups was used to determine the composition. The percentages of pendants which were originally silyl ketene acetals are shown in parentheses in column 1 of the Table. The latter were determined from the ratio of $-\text{CH}_2-$ resonance of the ethoxy group of the ketene acetal to that of the ester in the PSi-SKA-co-Ester. With the exception of sample A-3, the EA and NMR data are in reasonably good agreement. Conversions to the mono- or di-nitrothiophenoxy derivatives are high with the exception of the reaction between PSi-SKA and 2,4-dinitrobenzenesulfonyl chloride, which afforded only about 83% conversion to the dinitrothiophenoxy derivative.

Figures 4 and 5 summarize our DSC and dielectric constant data for the mononitro and dinitro copolymer series, respectively. Also included in these Figures are data for PSi-Ester. The steady increase in T_g in both series as the number of mono- or dinitrothiophenoxy groups increases is principally the result of increased dipole-dipole interactions between siloxane chains. The T_g 's of the dinitro series are higher than those of the mononitro series at a specific concentration of pendants, reflecting the higher polarity and/or larger molar volume of the dinitro thiophenoxy group. The dielectric constants at room temperature also increase with polar pendant group concentration, as expected, but then decrease for the most highly derivatized samples. We note that samples A-4 and B-4 (Table 2) have the highest T_g 's, and suggest that the dipoles cannot respond as effectively to the a.c. field at 100 kHz. An additional and probably dominant factor is dipole-dipole association in samples A-4 and B-4. It is well known, for example, that the dielectric constants of carboxylic acids are low at room temperature, due to dimer formation and subsequent cancellation of dipoles,⁹ and increase with temperature as the dimers are dissociated.⁷ The higher viscosity of the samples at lower temperatures may also assist dipole-dipole association. In order

to address this point, we have examined the dielectric constant of all samples except B-4 (due to its extremely high viscosity and difficulty in loading into the cell) as a function of temperature: the data are shown in Figure 6. Indeed, the dielectric constant of sample A-4 initially rises with temperature, as would be expected if dipole-dipole association was being disrupted. Similar behavior is exhibited by sample B-3, and it is interesting to note that A-4 and B-3 have similar T_g 's. The dielectric constants of A-4 and B-3 reach a maximum of about 10.2 at about 65°C, and then decrease with temperature. The latter is most likely due to randomization of dipoles with increasing temperature. The remaining samples show a steady decrease in dielectric constant with increasing temperature in the range studied. Apparently the concentration of nitro- or dinitrothiophenoxy groups in these is too low to promote dipole-dipole association. Cooling to room temperature in all cases restored the dielectric constants to their original values.

Dielectric loss tangents ($\tan \delta$'s or dissipation factors) of the samples at 100 kHz are shown in Figure 7 as a function of temperature. No obvious correlation exists between the magnitude of the loss tangent and composition at a given temperature. We do note, however, that loss tangents can be reasonably small (0.02-0.06) for selected samples.

Conclusions

Reactions of silyl ketene acetal-modified silicones with 4-nitrobenzenesulfonyl chloride or 2,4-dinitrobenzenesulfonyl chloride afford new silicones with high dielectric constants. The temperature dependencies of the dielectric constants are a function of polar pendant group concentration. It thus appears possible to design silicones with high dielectric constants as well as unique temperature dependencies.

Acknowledgements

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References

1. Wright, P. V. in "Ring Opening Polymerization" ,Vol.2, (Ivin K., Saegusa T., eds.) Elsevier, 1984, p. 1055.
2. Noll, W. "The Chemistry of Silicones," Academic Press, New York, 1968.
3. Yang, C.Y. and Wnek, G. E., *ACS Polymer Preprints*, 1989, **30**(2), 177.
4. Yang, C.Y. and Wnek, G. E., *ACS Polym. Mat. Sci. Eng. Prepr.*, 1990, **62**, 601.
5. Colvin, E. W., "Silicon in Organic Synthesis," Krieger, Malabar, FL, 1985, Ch. 17.
6. Webster, O. W., Hertler, W. R., Sogah, D. Y., Farnham, W. B. and RajanBabu, T. V., *J. Am. Chem. Soc.*, 1983, **105**, 570.
7. "Handbook of Chemistry and Physics," (ed. Weast, R). 55th ed., 1974/75, p. E-55.
8. Niki, F., Kamiya, Y. and Ohta, N., *Bull. Chem. Soc. Jpn.*, 1969, **42**, 3578.
9. S. J. Weininger, "Contemporary Organic Chemistry," Holt, Rinehart and Winston, New York, 1972, pp. 420-421.

Table 1. Data From Reactions of Dimethylmethoxy(trimethylsilyl)ketene Acetal with Electrophiles R-Cl

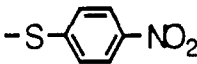
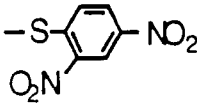
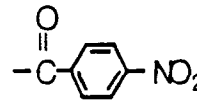
| R | Reaction time (hr) | % Conversion | MW theory/MS | mp or bp (c) |
|---|-----------------------|--------------|-----------------|---------------|
|  | 0.4 | 99 | 255.4/256 | 138-140/4mmHg |
|  | 0.7 | 95 | 300.3/301 | 82-86 (mp) |
|  | 2.4 | 95 | 251.3/252 | 62-64 (mp) |

Table 2: Elemental Analysis and Proton NMR Data for PSi-SKA and PSi-SKA-co-Ester Reacted with Either 4-nitrobenzenesulfonyl chloride (mononitro series, labeled as A) or 2,4-dinitrobenzenesulfonyl chloride (dinitro series, labeled as B).

| Sample | NMR | EA |
|-----------|------|------|
| A-1 (32) | 27.3 | 26.7 |
| A-2 (48) | 46.4 | 47.0 |
| A-3 (69) | 63.3 | 56.6 |
| A-4 (100) | 95.5 | 92.7 |
| B-1 (31) | 24.6 | 26.3 |
| B-2 (49) | 44.5 | 44.5 |
| B-3 (69) | 61.7 | 57.6 |
| B-4 (100) | 81.8 | 83.8 |

Figure Captions

- Figure 1. 200 MHz ^1H NMR spectra of a.) PMHS, b.) PSi-SKA, c.) PSi-Ester.
- Figure 2. 200 MHz ^1H NMR spectrum of sample A-3.
- Figure 3. 200 MHz ^1H NMR of sample A-4.
- Figure 4. Change of dielectric constant and glass transition temperature with nitrothiophenoxy concentration for Samples A-1 through A-4.
- Figure 5. Change of dielectric constant and glass transition temperature with 2,4-dinitrothiophenoxy concentration for Samples B-1 through B-4.
- Figure 6. Temperature dependence of dielectric constant for all samples at 100 kHz.
- Figure 7. Dielectric dissipation factor ($\tan\delta$'s) for all samples at 100 kHz as a function of temperature.

Figure 1b

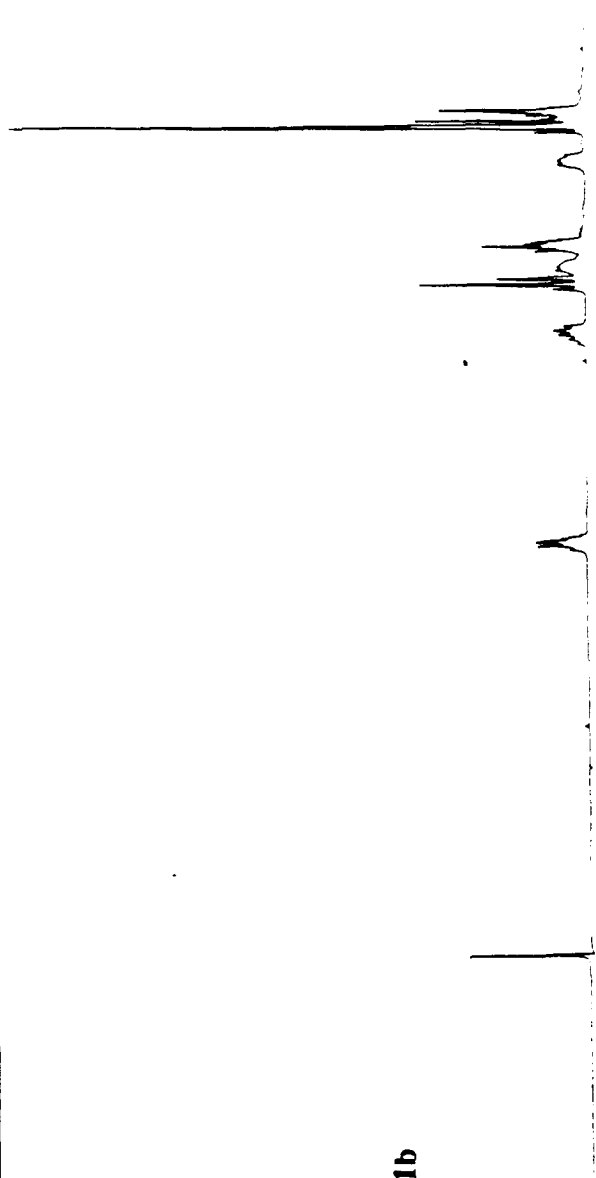


Figure 1a

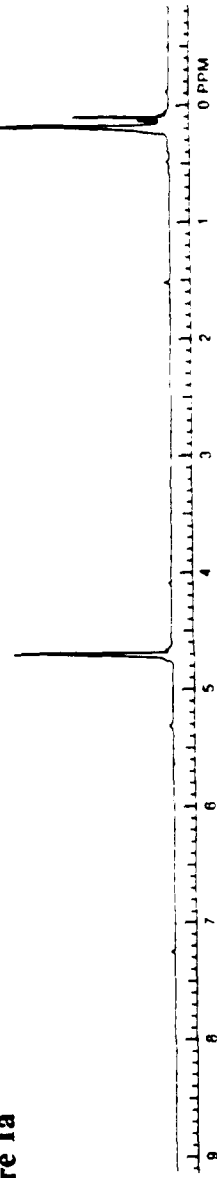
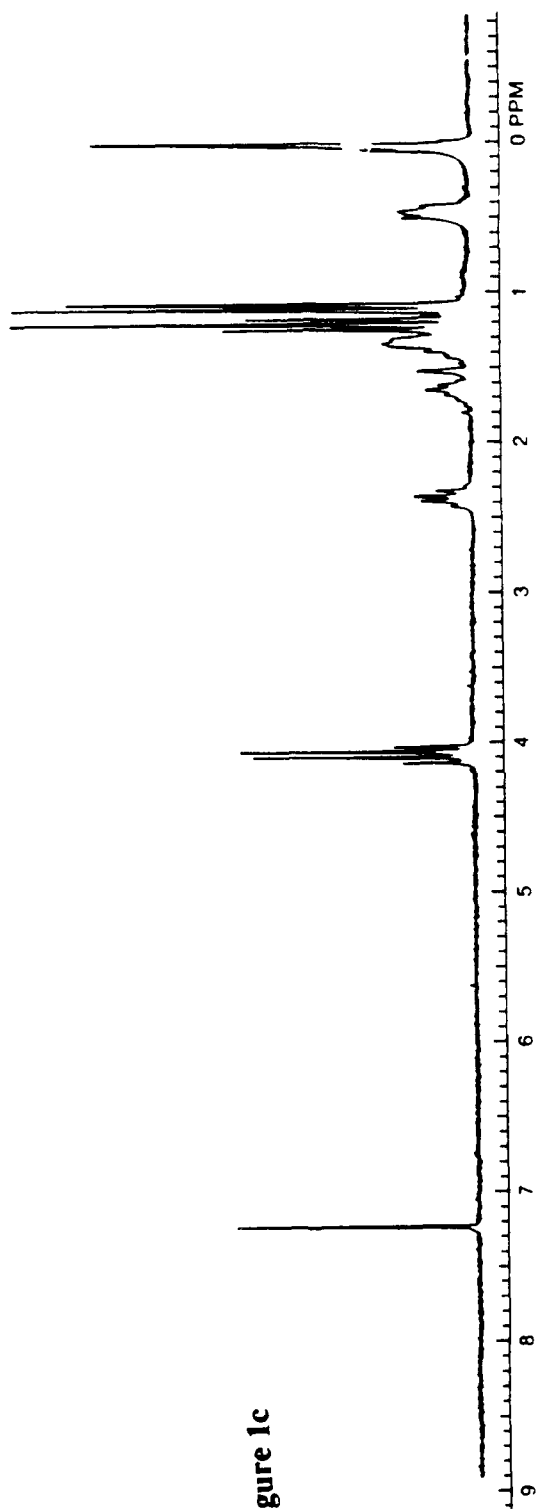


Figure 1c



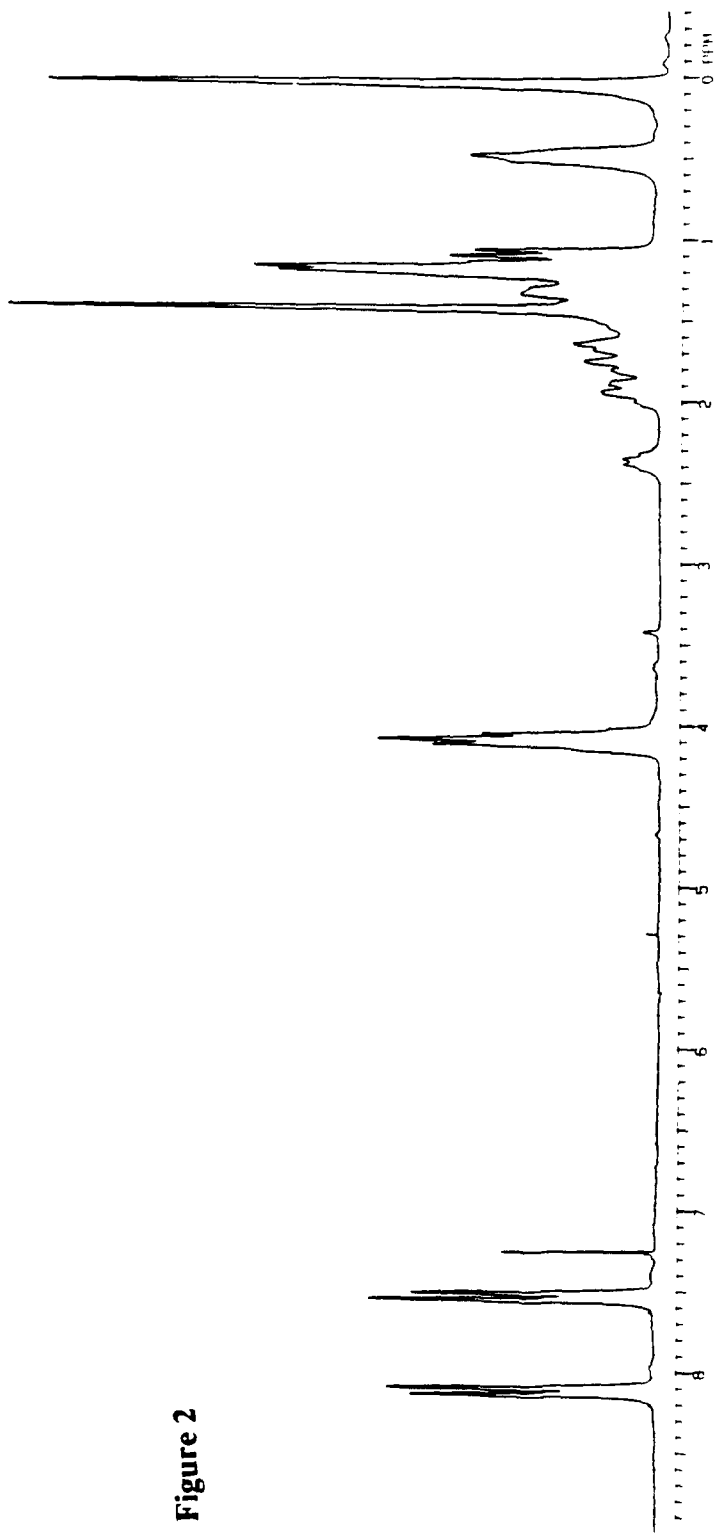


Figure 2

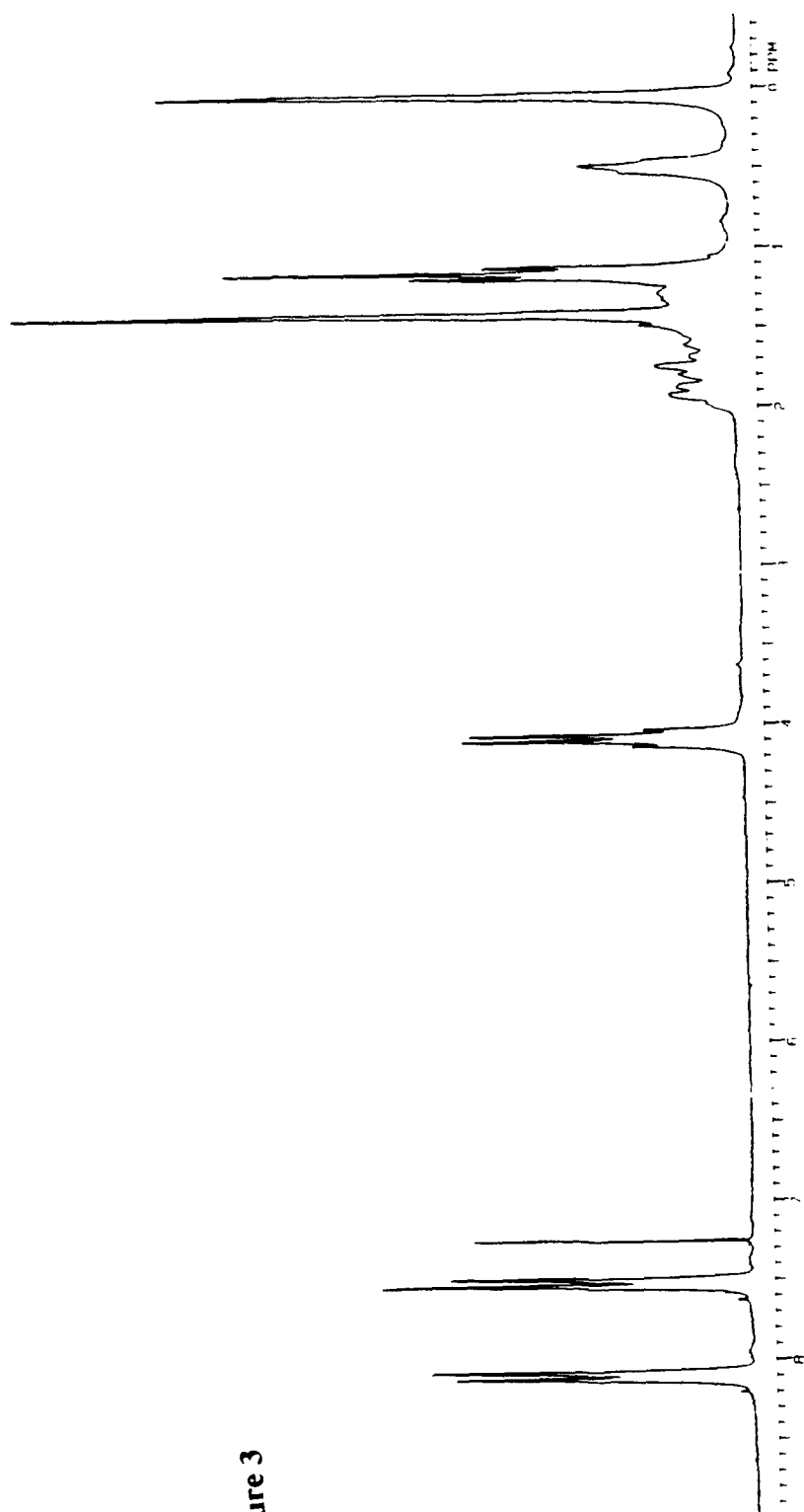


Figure 3

Figure 4

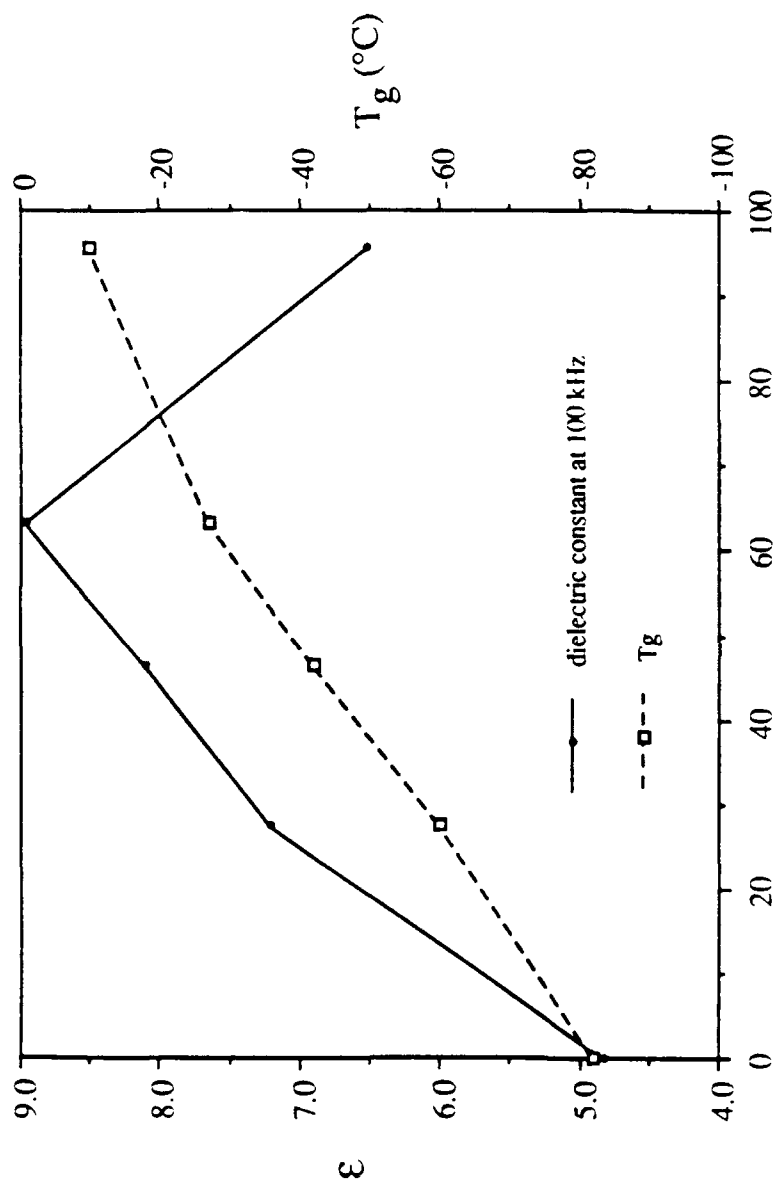


Figure 5

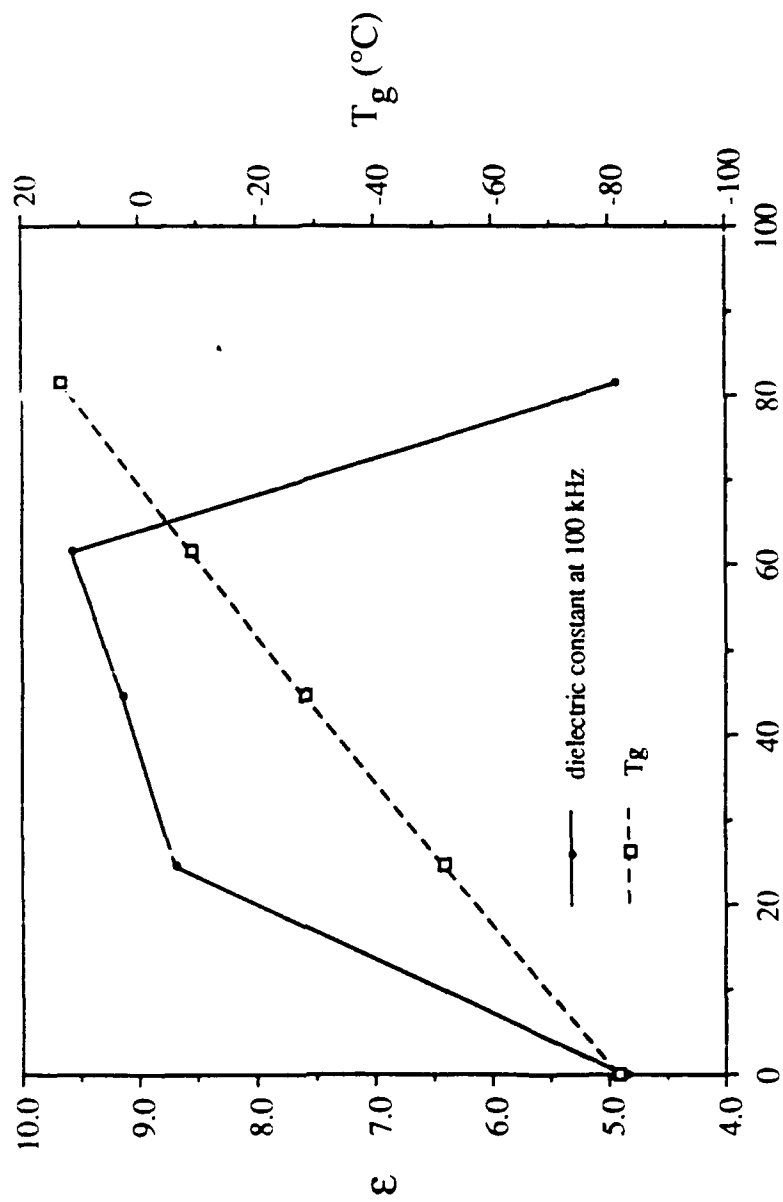


Figure 1 is a line graph showing the variation of dielectric constant (ϵ) with temperature ($^{\circ}\text{C}$) for seven different samples: A1(100kHz), A2(100kHz), A3(100kHz), A4(100kHz), B1(100kHz), B2(100kHz), and B3(100kHz). The y-axis represents ϵ , ranging from 5.0 to 11.0. The x-axis represents Temperature ($^{\circ}\text{C}$), ranging from 20 to 120. All samples show a characteristic peak in ϵ around 30-40°C, followed by a decrease and then a gradual increase at higher temperatures. The peak values range from approximately 8.5 to 10.5.

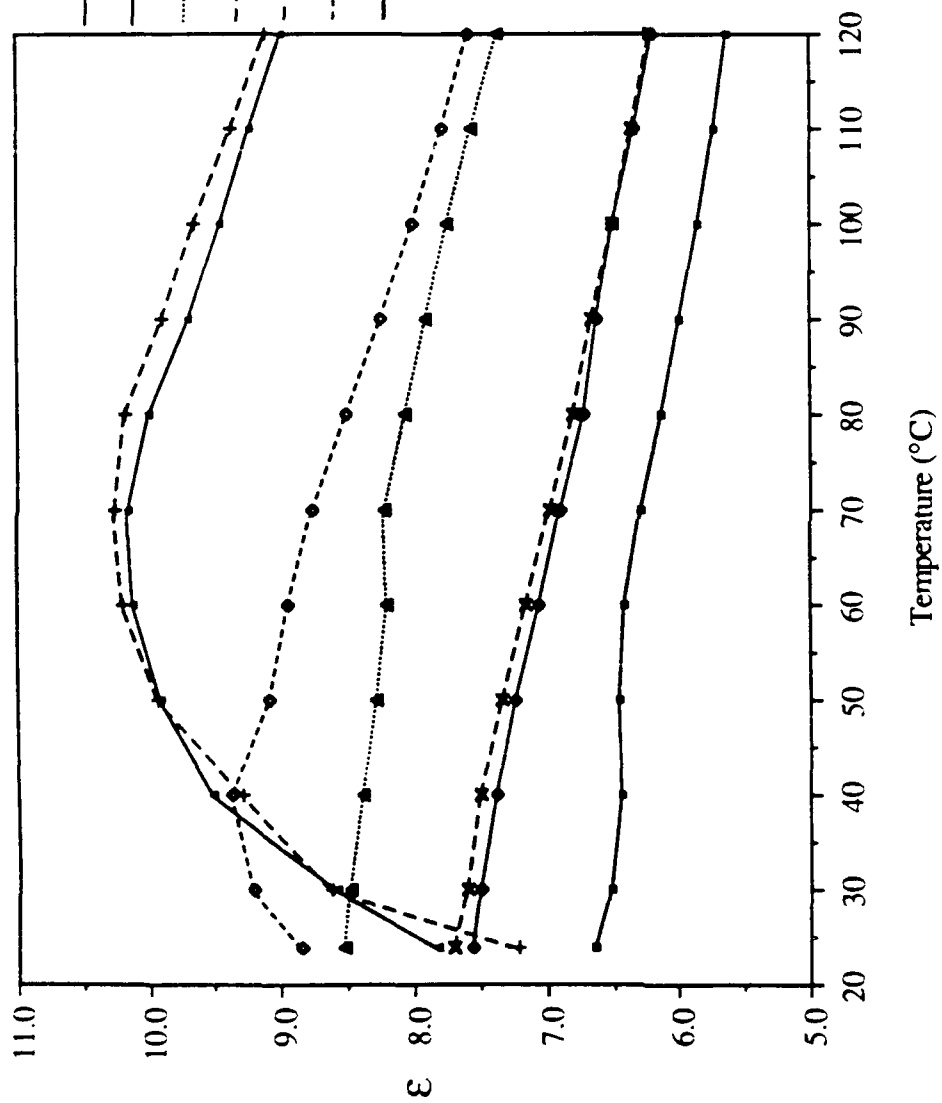


Figure 7

